

# PATENT SPECIFICATION

(11) 1 576 217

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- (21) Application No. 54129/76 (22) Filed 24 Dec. 1976  
 (31) Convention Application No. 2 558 813  
 (32) Filed 27 Dec. 1975 in  
 (33) Fed. Rep. of Germany (DE)  
 (44) Complete Specification published 1 Oct. 1980  
 (51) INT CL<sup>3</sup> C08F 2/50; G03C 1/68, 1/71  
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 C3P 402 408 414 504 510 528 538 540 544 546 HL  
 G2C 1A1 1D3D 1E1F 1G1 1G3 1G5 1G7 1GX C6A



## (54) LIGHT-SENSITIVE COMPOSITIONS

(71) We, HOECHST AKTIENGESellschaft, a Body Corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to light-sensitive compositions which may be supplied either in the form of solid layers or as liquid preparations and which comprise at least one ethylenically unsaturated polymerizable compound and a photoinitiator system and, optionally, at least one polymeric binder.

Within the term "ethylenically unsaturated polymerizable compounds" there are included low molecular weight polyfunctional monomers capable of addition polymerization and polyunsaturated high molecular weight compounds that can be photocrosslinked.

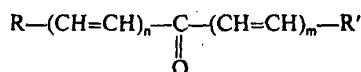
Substances belonging to the most varied classes of compounds have been proposed as photoinitiators for the photopolymerization of unsaturated compounds. It has been proposed to use as photoinitiators, for example, chalcones, aromatic ketones or diketones, multi-nuclear quinones of the anthraquinone or phenanthrenequinone type, benzanthrone derivatives or aza-benzanthrone derivatives, aromatic nitro compounds, heterocyclic six-membered compounds, such as acridines, phenazines, quinoxalines, quinazolines, pyrylium compounds and thia-pyrylium compounds, heterocyclic five-membered compounds, e.g. benzthiozoles, benzoxazole, or benzimidazoles, and oranic dyestuffs, e.g. eosin, methylene blue or fuchsine.

Due to their molecular structure, these photoinitiators very often can be used only for particular layers and substantially lose their effectiveness when used in other polymerizable compositions.

In many cases, it is necessary to use a considerable quantity of the initiator in order to achieve high cross-linking densities, and in these cases the applicability of the initiator is limited by its solubility in the light-sensitive compositions.

Lack of compatibility is frequently observed when the copying composition is subjected to substantial variations in temperature under unfavorable conditions of storage or transport. Under these conditions, exudation and/or crystallization of the photoinitiator may occur, which result in a loss of light-sensitivity, sometimes considerably impair the adhesion of the light-sensitive layer to a support therefor and substantially detract from the shelf-life of the copying composition.

It has been proposed in German Offenlegungsschrift No. 2 060 575, to use unsaturated ketones of the type



as photoinitiators in compositions containing monomers with vinyl or vinylidene groups. The light-sensitivity of layers containing only such compounds is not really satisfactory, even if relatively large quantities of photoinitiator are used nor does their use in combination with special compounds known to be suitable photoconductors from German Patent No. 1 137 625, e.g. appropriately substituted multi-nuclear heterocyclic compounds having groups displaying an electron-donor

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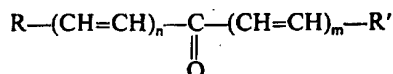
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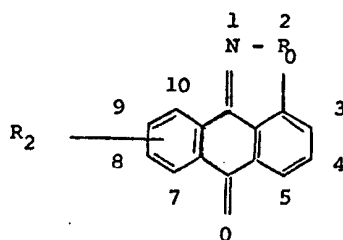


as photoinitiators in compositions containing monomers with vinyl or vinylidene groups. The light-sensitivity of layers containing only such compounds is not really satisfactory, even if relatively large quantities of photoinitiator are used nor does their use in combination with special compounds known to be suitable photoconductors from German Patent No. 1 137 625, e.g. appropriately substituted multi-nuclear heterocyclic compounds having groups displaying an electron-donor

effect, meet the demands for high light-sensitivity combined with high cross-linking density made on photoresist materials which must be resistant to corrosive electroplating baths.

It is the object of the present invention to provide a photoinitiator system of good compatibility with the other ingredients of the light-sensitive compositions, which is especially suitable for the photopolymerization of low molecular weight monomeric acrylates and alkylacrylates, and which imparts to the composition good light-sensitivity in combination with a high cross-linking density.

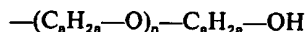
The present invention provides a light-sensitive composition comprising at least one liquid or solid ethylenically unsaturated compound having at least two, preferably terminal, double bonds capable of addition polymerization, other than a compound of the formula II, and a photoinitiator system comprising at least one compound of the general Formula I



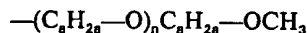
wherein

$R_0$  is O, S, or  $NR_1$ ,

$R_1$  denotes hydrogen, a saturated or unsaturated unsubstituted hydrocarbon radical with 1 to 6 carbon atoms, an aminocarbonyl group with from 2 to 11 carbon atoms, an aralkyl group with 7 to 10 carbon atoms, an acyl group with 2 to 18 carbon atoms, an amidomethylene group or a polyalkyleneoxide group of the general formula

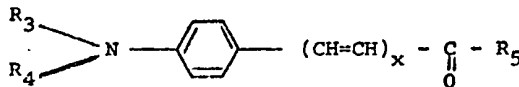


or the general formula



wherein  $a=2$  to 4 and  $n=1$  to 10, or a saturated or unsaturated hydrocarbon radical with 1 to 6 carbon atoms which is substituted by hydroxyl, alkoxy, alkoxy carbonyl, acyl, acyloxy, and/or halogen,

$R_2$  is hydrogen, an alkoxy group, an alkyl group with 1 to 6 carbon atoms, or halogen, and at least one compound of the general Formula II



wherein

$R_3$  is an alkyl group with 1 to 6 carbon atoms,

$R_4$  is an alkyl group with 1 to 6 carbon atoms, and

$R_5$  is hydrogen, an alkyl group with 1 to 6 carbon atoms, an alkoxy group in which the alkyl group has 1 to 4 carbon atoms, an aryl group with 6 to 12 carbon atoms, or a dialkyl amino styryl group, and wherein

$x$  is 0 or 1, and, optionally, at least one polymeric binder.

The compounds corresponding to the 6-oxo-anthra(1,9-cd)pyrazole-2(6H) type (Formula I;  $R_0=NR_1$ ) are advantageously substituted in the 2-position ( $=R_1$ ) by hydrogen, unsubstituted alkyl groups with 1 to 6, preferably 2 to 4 carbon atoms, hydroxyl, alkoxy, alkoxy carbonyl preferably ethoxy carbonyl, acyl or halogen, preferably chlorine or bromine, or by substituted alkyl groups with 1 to 6, preferably 2 to 2 carbon atoms, the numbers 1 to 6 designating the number of carbon atoms arranged in a straight chain in the substituted alkyl group.

Further suitable substituents in the 2-position are: the allyl group, an aralkyl group with 7 to 10 carbon atoms, preferably benzyl or tolyl, or an acyl group with 2 to 18 carbon atoms. Among the acyl groups, acetyl to stearyl, benzoyl, methoxybenzoyl, ethoxy benzoyl, methyl benzoyl, benzsulfonyl, or tosyl are preferred.

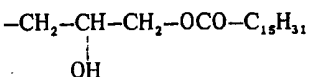
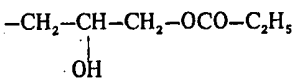
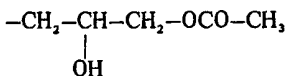
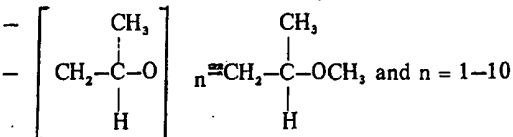
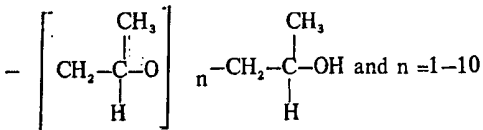
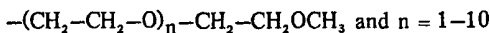
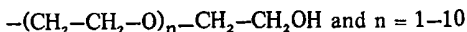
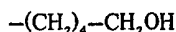
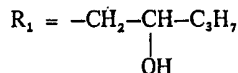
The substituent  $R_2$  in the six-membered ring of the basic anthracene structure (Formula I;  $R_0=O, S, NR_1$ ) may be in the 7, 8, 9, or 10-position, preferably in the 10-position, and may be hydrogen, halogen, preferably chlorine or bromine, or alkoxy, preferably methoxy or ethoxy, or alkyl with 1 to 6 carbon atoms, preferably methyl or ethyl.

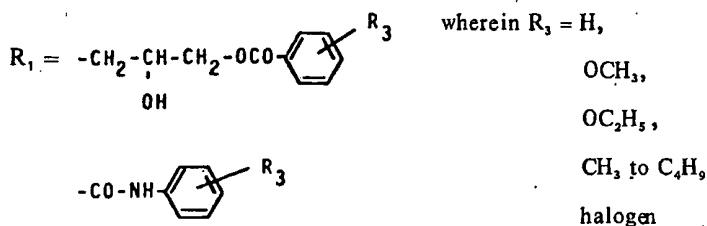
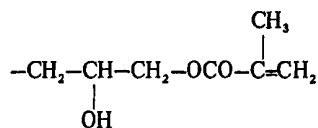
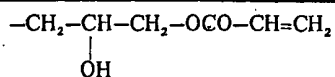
Suitable substituents for  $R_3$  and  $R_4$  in compounds of the type of Formula II are lower unsubstituted alkyl groups with 1 to 6, preferably 1 to 4 carbon atoms, which may be arranged in a straight chain or branched;  $R_3$  and  $R_4$  may be the same or different.

The substituent in  $R_5$  may be hydrogen, a lower alkyl group with 1 to 6, preferably 1 to 4 carbon atoms, an alkoxy group, preferably methoxy, ethoxy, isopropoxy, propoxy or butoxy, an unsubstituted aryl group with 6 to 12 carbon atoms, preferably phenyl, or a substituted aryl group, preferably tolyl, dialkylaminophenyl, or anisyl, or a dialkylamino styryl group.

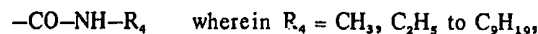
As indicated above, x may be 0 or 1, but is preferably 0.

Compounds corresponding to the Formula I, wherein  $R_0$  stands for  $N-R_1$ , may contain, for example, any of the following groups as substituents in the 2-position:

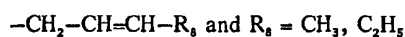
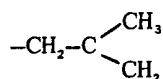
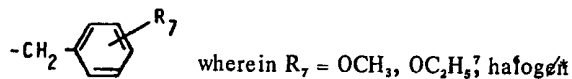
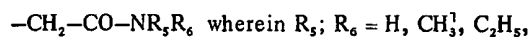




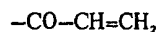
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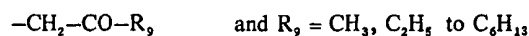
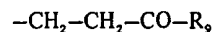
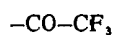
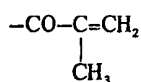
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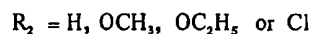


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15 and wherein

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The following Tables I and II list preferred compounds of the Formulae I and II, respectively:—

TABLE I

No. of the Compound	Substituent R <sub>0</sub>	Substituent R <sub>1</sub>	Substituent R <sub>2</sub>
I 1	O	—	H
I 2	S	—	H
I 3	NR <sub>1</sub>	H	H

TABLE I — Continued.

No. of the Compound	Substituent $R_0$	Substituent $R_1$	Substituent $R_2$
I 4	$NR_1$	$CO-C_6H_5$	H
I 5	$NR_1$	$CO-C_6H_4\cdot p-OCH_3$	H
I 6	$NR_1$	$CO-C_{17}H_{35}$	H
I 7	$NR_1$	$CO-C_7H_{16}$	H
I 8	$NR_1$	$CO-C_3H_7$	H
I 9	$NR_1$	$CO-C_2H_5$	H
I 10	$NR_1$	$CO-CH_3$	H
I 11	$NR_1$	$SO_2-C_6H_4\cdot p-CH_3$	H
I 12	$NR_1$	$n-C_4H_9$	H
I 13	$NR_1$	$i-C_4H_9$	H
I 14	$NR_1$	Allyl	H
I 15	$NR_1$	Benzyl	H
I 16	$NR_1$	$CH_2-COOC_2H_5$	H
I 17	$NR_1$	$CH_2-CO-C_6H_5$	H
I 18	$NR_1$	$CH_2CH(OH)CH_2CH_3$	H
I 19	$NR_1$	H	$OC_2H_5$
I 20	$NR_1$	$CO-C_6H_5$	$OC_2H_5$
I 21	$NR_1$	$CO-C_6H_4\cdot p-OCH_3$	$OC_2H_5$
I 22	$NR_1$	$CO-C_{17}H_{35}$	$OC_2H_5$
I 23	$NR_1$	$CO-C_7H_{15}$	$OC_2H_5$
I 24	$NR_1$	$CO-C_2H_5$	$OC_2H_5$
I 25	$NR_1$	$CO-CH_3$	$OC_2H_5$
I 26	$NR_1$	Benzyl	$OC_2H_5$
I 27	$NR_1$	$CH_2-CO-O-C_2H_5$	$OC_2H_5$
I 28	$NR_1$	$CH_2-CO-C_6H_5$	$OC_2H_5$
I 29	$NR_1$	$CH_2-CH(OH)-CH_2-CH_3$	$OC_2H_5$
I 30	$NR_1$	H	Cl
I 31	$NR_1$	$CH_2-CH(OH)CH_2CH_3$	Cl
I 32	$NR_1$	$CH_2-CH(OH)-CH_2Cl$	Cl
I 33	$NR_1$	$CO-CH_3$	Cl

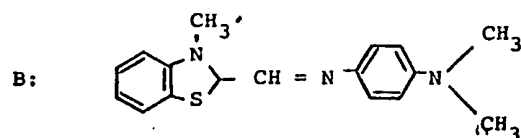
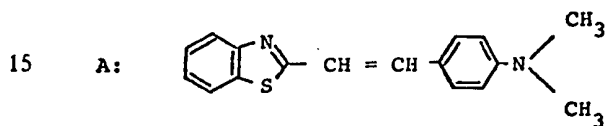
TABLE II

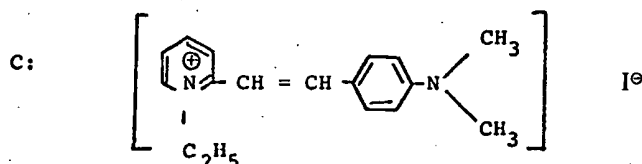
No. of the Compound	Substituents R <sub>3</sub>	Substituents R <sub>4</sub>	Substituent R <sub>5</sub>	x
II 1	CH <sub>3</sub>	CH <sub>3</sub>	p-C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	0
II 2	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>3</sub>	0
II 3	CH <sub>3</sub>	CH <sub>3</sub>	OCH <sub>2</sub> CH <sub>3</sub>	0
II 4	CH <sub>3</sub>	CH <sub>3</sub>	O-i-C <sub>3</sub> H <sub>7</sub>	0
II 5	CH <sub>3</sub>	CH <sub>3</sub>	OC <sub>4</sub> H <sub>9</sub>	0
II 6	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	0
II 7	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	0
II 8	CH <sub>3</sub>	CH <sub>3</sub>	i-C <sub>3</sub> H <sub>7</sub>	0
II 9	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	0
II 10	CH <sub>3</sub>	CH <sub>3</sub>	H	0
II 11	CH <sub>3</sub>	CH <sub>3</sub>	CH=CH-C <sub>6</sub> H <sub>4</sub> -p-N(CH <sub>3</sub> ) <sub>2</sub>	1
II 12	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	1
II 13	CH <sub>3</sub>	CH <sub>3</sub>	p-C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	1
II 14	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	0
II 15	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	p-C <sub>6</sub> H <sub>4</sub> -N-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0

Surprisingly, it has been found that, by combining a compound of the Formula I with a compound of the Formula II a light-sensitivity is achieved which in some cases exceeds the sum of the individual effects of the components used by one order of magnitude or more, as expressed, e.g., by the number of fully reproduced steps of a step wedge. That is to say that, in some cases, a synergistic effect is in operation.

Although all compounds of Formula II contain a p-dialkylaminophenyl group, the presence of this group is not alone sufficient to predict a synergistic effect for compounds of this type.

This is demonstrated by the fact, that the compound I 18, for example, does not form a synergistic photoinitiator combination with the following compounds A, B or C. The effectiveness of the compound I 18 is either not increased by these compounds (A, B), or is even reduced (C):





Thus, the marked increase in the photoinitiator effect of the compounds of the Formula I when combined with compounds of Formula II is the more surprising.

The synergistic effect is very pronounced at all mixing ratios, as can be clearly seen from Example 4 below.

The proportions by weight of the compounds of Formula I and Formula II used according to the invention may vary within wide limits and preferably range from 2:98 to 98:2. Proportions between 80:20 and 20:80 are more preferred, and within these limits proportions from 40:60 to 60:40.

Examples of suitable polymerisable compounds are, for example, acrylic and methacrylic acid esters, especially the commercially available ones, for example those of diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, trimethylolpropane and trimethylolpropane; diglycerol diacrylate, guaiacol glycerol ether diacrylate, neopentyl glycol diacrylate, 2,2-dimethylol butanol-(3)-diacrylate, unsaturated pentaerythritol esters, as described in U.S. Patent 3,261,686, reaction products of trimethylol-propane, alkylene oxide and acrylic acids or methacrylic acids in accordance with U.S. Patent No. 3,380,831, and acrylates and methacrylates of polyesters containing hydroxy groups. The latter compounds and other compounds suitable for use in the compositions are described in, for example, U.S. Patents Nos. 2,760,863 and 3,060,023.

The compounds containing urethane groups described in German Offenlegungsschrift No. 2,064,079 and the biuret-group



containing compounds described in German Offenlegungsschrift No. 2,361,041 are also examples of suitable polymerisable compounds.

As will be appreciated the present invention is not limited to the use of specific polymerizable compounds; all that is necessary is that the compound be at least twice ethylenically unsaturated and capable of addition polymerization or be a polyunsaturated, high molecular weight compound that is either capable of being photocrosslinked, or capable of addition polymerization with a low molecular weight compound. The following polyunsaturated compounds, for example, are suitable for use in light-sensitive compositions:

Polyvinyl cinnamates and prepolymers of unsaturated esters, e.g. the prepolymer of diallyl isophthalate, or the polymeric allyl imides described in German Offenlegungsschrift No. 2,203,732, and the polyvinyl acetals containing extralinear vinylidene groups according to U.S. Patent No. 2,902,710.

The polymerisable compounds preferably contain small amounts (e.g. 50 to 100 ppm) of an inhibitor in order to prevent thermally induced polymerization.

If the copying compositions according to the invention are to survive extreme conditions of storage without deterioration, the quantity of inhibitor may be increased to about 1 per cent, calculated on the weight of the polymerisable compound used.

The following compounds may, for example, be used as thermal inhibitors: p-Methoxyphenyl, hydroquinone, alkyl-substituted or aryl-substituted quinones and hydroquinones, tertiary butyl catechol, pyrogallol, copper resinate, naphthyl amine, β-naphthol, copper-(I)-chloride, 2,6-di-tert.-butyl-p-cresol, phenothiazine, pyridine, nitrobenzene, and dinitrobenzene; p-toluquinone, chloroanil and thiazine dyestuffs, for example Thionine Blue G.

The light-sensitive compositions optionally comprise one or more binders, and normally will do so when the polymerisable compound is a liquid, for example solvent-soluble polyamides, polyvinyl acetates, polymethyl(meth)-acrylates, polyvinyl butyrals, cellulose ethers or cellulose esters, polyalkylene ethers, condensation polymers of glycols with dibasic acids, copolymers of styrene and maleic anhydride which are soluble or at least swellable or softenable in alkaline solutions, copolymers of ethylene and maleic anhydride or of alkyl methacrylates



and methacrylic acid, for example as described in German Offenlegungsschrift No. 2,064,080, terpolymers of styrene, alkylmethacrylates, and methacrylic acid, for example as described in German Offenlegungsschrift No. 2,363,806, copolymers of methyl methacrylate and N-(p-toluene-sulfonyl)-carbamic acid-( $\beta$ -methacryloxy)-ethylester, for example as described in German Offenlegungsschrift No. 2,027,466, further maleate resins, terphenol resins, and others.

Aqueous alkaline developers are preferably used for development and, therefore, binders are preferred which are either alkali-soluble or softenable in aqueous alkaline solutions. Examples of such binders are copolymers of styrene and maleic anhydride and copolymers of alkyl methacrylate and methacrylic acid, terpolymers of styrene, alkyl methacrylate and methacrylic acid, maleic resins, and the copolymers described in German Offenlegungsschrift No. 2,205,046.

Further, plasticizers, adhesion promoters, hydrogen donors, oxygen absorbants, dyestuffs, pigments, color couplers, UV-absorbing substances and sensitometric regulators, for example, may be included in the compositions of the invention.

The type and quantity of these additives are determined by the field of application for which the copying composition is destined. Further, care must be taken that the substances added do not absorb an undue proportion of the actinic light required for the initiating process and thus reduce the practical light-sensitivity of the copying composition.

Suitable plasticizers are, for example, dibutyl phthalate, diisooctyl adipate, nitrate esters, alkyl and aryl phosphate esters, chlorinated paraffines, glycols and aliphatic polyols. If good storability at high atmospheric moisture is to be ensured, water-insoluble plasticizers are preferably used.

Adhesion promoters are preferably added in cases where the light-sensitive copying compositions are to be exposed to extreme stress, for example when they are to be used as photoresist materials. The following adhesion promoters have been found to be advantageous in such cases:— monomeric or polymeric organic silanes, nitrogen-containing heterocyclic compounds, for example those described in U.S. Patents No. 3,645,722, No. 3,622,234 and No. 3,827,908, heterocyclic mercaptans, for example those described in German Offenlegungsschrift No. 2,028,773, mercapto alkanic acid anilides, for example those described in German Offenlegungsschrift No. 2,448,821, and mercapto alkanoic acid esters, for example those described in German Offenlegungsschrift No. 2,448,850.

Suitable hydrogen donors are, for example, substances containing aliphatic ether groups or cyclic  $\beta$ -di-carbonyl compounds. In some cases, the binder or the polymerizable substance may be capable of effecting this function, provided it contains a labile hydrogen atom.

Further, the compositions of the invention may comprise dyestuffs and/or pigments, which may be added in order to enhance the contrast or to solidify the layer. Suitable dyestuffs are described, for example, in U.S. Patents Nos. 3,218,167 and 3,884,693.

The light-sensitive copying compositions of the invention may further contain U.V. absorbers serving as anti-halation filters. Suitable non-coloring substances are described, for example, in German Offenlegungsschrift No. 2,243,182.

The following proportions of various components of the light-sensitive copying compositions are preferred, the percentages being by weight and being calculated on the total solids content of the compositions:

binder:	15—99 per cent
monomer:	1—75 per cent
photoinitiator mixture:	0.1—10 per cent
hydrogen donor:	0.5—10 per cent
plasticizer:	0.0—15 per cent
adhesion promoter:	0.0—15 per cent
dyestuff or pigment:	0.0—30 per cent.

For commercial purposes, the light-sensitive copying compositions may be supplied in the form of solutions or dispersions, i.e. as so-called photoresist lacquers, which the customer himself applies to a particular support — this being the usual procedure, for example, for chemical milling, for the preparation of printed circuits or stencils, or for making printing plates and screen printing stencils — followed by drying, imagewise exposure and development. In this case, the ingredients of the light-sensitive copying composition are dissolved in a suitable solvent. Suitable solvents are, for example, alcohols, ketones, esters, ethers, amides and hydrocarbons. The partial ethers of glycols or of keto-alcohols have proved to be particularly favorable solvents but the choice of solvent is substantially determined by the binder, if any, present in the composition.

Alternatively, the light-sensitive copying compositions may be marketed in the form of a solid photopolymerizable layer disposed on a support and may be used as such for the preparation of, for example, printing forms, relief images, etch resists, stencils, matrices, screen printing forms or single copies. A particularly important application is as storable pre-sensitized printing plates processable into planographic, relief or intaglio printing formes.

The supports are coated with the compositions from appropriate organic solvents or solvent mixtures, using, for example, casting, spraying or immersion processes. Suitable supports comprise, for example, magnesium, zinc, copper, mechanically, chemically or electrochemically roughened aluminium, anodized aluminium, steel, polyester or acetate films, polyamide, e.g., "Perlon" gauze, the surfaces of which may be subjected to a pre-treatment, where necessary. The support may serve either as the final, permanent, support or as an intermediate support from which the light-sensitive copying composition is transferred, by lamination, onto the workpiece to be processed. If thick photopolymer layers are to be produced, i.e. of a thickness of several tenths of a millimetre, the copying composition may be kneaded without dissolution, for example in a three-roll mill, and then hydraulically pressed onto the support, for example for one minute at a pressure of 30,000 to 50,000 kp and a temperature of 90°C.

If crosslinking is effected solely by polymerization of the ethylenically unsaturated compound(s), it is normally of advantage to protect the light-sensitive copying composition, during exposure, from atmospheric oxygen, because oxygen tends to intercept the radicals forming within the layer and to deactivate them. Such an exclusion of oxygen may be achieved by providing the light-sensitive layer with an oxygen-impermeable barrier layer, as is described, for example, in German Offenlegungsschriften Nos. 1,572,153 and 2,036,585.

If the light-sensitive copying composition contains a high molecular weight compound which is capable of a photochemical crosslinking reaction, so that crosslinking is not exclusively or predominantly caused by, for example, low molecular weight acrylates or alkyl acrylates, no such barrier layer is necessary, because in this case photo-crosslinking results in the desired differentiation between exposed and unexposed areas even in the presence of oxygen.

Material prepared with the light-sensitive copying compositions according to the invention may be used, on the one hand, for the preparation of images on suitable support or receiving sheets, and, on the other hand, for the preparation of relief images which may be used, for example, as printing forms, screens, and photoresists. In addition, it is possible for the light-sensitive copying compositions of the present invention to be used for the preparation of UV-hardening lacquers which may be used for surface protection, or for the preparation of UV-hardening printing inks which do not dry physically and do not cross-link chemically, with formation of cross-connections by oxygen action. Drying is by a photochemical process and thus is particularly fast and ecologically safe.

Printing forms, screens, and etch resists may be prepared from appropriate copying materials according to the invention in the usual manner, e.g. after exposure to actinic light through a suitable original the non-image areas are removed by treatment with suitable solvents, e.g. aqueous alkaline solutions, in which those areas are soluble but in which the image areas, by virtue of their being hardened by the action of the light, are insoluble.

Alternatively, development may be effected by other methods, utilizing other physical differences between the hardened image areas and the unhardened non-image areas, for example differences in their melting points, their stickiness, their adhesiveness or their optical transparency.

The invention is illustrated by some of the following Examples. Other

The relation between parts by weight and parts by volume is the same as that between grams and milliliters.

**Example 1.**

10	1.5 p.b.w. of tri-[4-(methyl-phenylamino)-phenyl]-methyl acetate	10
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15 to Formula I and 3.5 p.b.w. of an initiator according to Formula II are added. 15

After drying, the sample plates are so coated with an aqueous solution

20	2.0 p.b.w. of carboxy methyl cellulose,	20
----	---	----

1.0 p.b.w. of saponin, and

267.0 p.b.w. of water,

exposed for two minutes under a 21-step half-tone wedge with a density range of

2). The light source used is an 8,000 W "Xenokop" spot arc lamp (distance: 72 cm).

30 with a developer having a pH of 11.9 and being composed of: 30

0.3 p.b.w. of polyethylene glycol 6000,  
0.06 p.b.w. of levulinic acid, and

35 0.03 p.b.w. of strontium hydroxide octahydrate in 100.0 p.b.w. of water 35

If the copying layers are processed in this manner, the fully reproduced steps

40 initiator mixtures tested, i.e. the higher the number of steps reproduced, the higher the practical light-sensitivity. 40

wedge for each of the initiator combinations tested, adjacent partially colored

the step wedge differ by a factor of  $\sqrt{2}$ . Step 0 of the step wedge corresponds to an

\* "Kodak is a trade mark

TABLE III

Initiators		Test No.	Number of Steps
Type I	Type II		
I 9		1	1
I 14		2	1
I 15		3	3
	II 1	4	1
	II 3	5	0
	II 6	6	0
	II 9	7	0
	II 15	8	1
I 9	II 1	9	7
I 9	II 3	10	8
I 9	II 6	11	9
I 9	II 9	12	6
I 9	II 15	13	3
I 14	II 1	14	6
I 14	II 3	15	10
I 14	II 6	16	10
I 14	II 9	17	7
I 14	II 15	18	5
I 15	II 1	19	8
I 15	II 3	20	8
I 15	II 6	21	8
I 15	II 9	22	9
I 15	II 15	23	4

## Example 2.

This example shows the influence of different compounds of Formula II on a specific compound of Formula I (Compound No. I 18).

5 140.0 p.b.w. of a copolymer of 85 p.b.w. of methyl methacrylate and 15 p.b.w. of methacrylic acid with an average molecular weight of 43,000 and an acid number of 86,

140.0 p.b.w. of trimethylol ethane triacrylate, and

10 1.5 p.b.w. of a blue azo dyestuff, obtained by coupling 2,4-dinitro-6-chloro-benzene-diazonium salt with 2-methoxy-5-acetylamino-N-cyano-ethyl-N-hydroxy-ethyl aniline,

are dissolved in

1400.0 p.b.w. of ethylene glycol monoethyl ether.

A series of such solutions are prepared and to each of them either 5.0 p.b.w. of

5

10

one initiator, or 2.5 p.b.w. of the initiator corresponding to Formula I 18 and 2.5 p.b.w. of one of the initiators corresponding to Formula II are added.

The solutions are filtered and whirler-coated, at 100 revolutions per minute, onto an electrochemically roughened and anodized aluminum foil.

5

The dried samples are coated with a solution of

5

3.5 p.b.w. of polyvinyl alcohol and

1.0 p.b.w. of sodium lauryl-ether-sulfate in

96.5 p.b.w. of water

10

which has a viscosity of about 16 cp and are then dried. Further processing is as described in Example 1. Table IV indicates the relative light-sensitivities of the samples obtained.

10

TABLE IV

Initiators		Test No.	Number of Steps
Type I	Type II		
I 18		24	1
	II 14	25	0
	II 11	26	0
	II 2	27	no image
	II 15	28	0
	II 12	29	0
	II 13	30	0
	II 6	31	0
I 18	II 14	32	7
I 18	II 11	33	4
I 18	II 2	34	12
I 18	II 15	35	8
I 18	II 12	36	5
I 18	II 13	37	6
I 18	II 6	38	11

## Example 3.

15

This example serves to show the influence of one initiator compound of Formula II upon different initiator compounds of Formula I.

The tests were carried out analogously to Example 2. Several compounds were used as initiators corresponding to Formula I, and the Initiator of Formula II was the compound numbered II 1.

The results are listed in the following Table V.

15

TABLE V

Initiators		Test No.	Number of Steps
Type I	Type II		
I 1		39	1
I 9		40	5
I 17		41	4
I 18		42	1
I 28		43	0
	II 1	44	1
I 1	II 1	45	10
I 9	II 1	46	12
I 17	II 1	47	12
I 18	II 1	48	11
I 28	II 1	49	8

## Example 4.

This example shows how wide the limits in which the mixing ratio of the two components of the initiator system may be varied without losing its synergistic effect.

140.0 p.b.w. of a copolymer of 85 p.b.w. of methyl methacrylate and 15 p.b.w. of methacrylic acid with an approx. average molecular weight of 43,000,

140.0 p.b.w. of trimethylol ethane triacrylate, and

1.5 p.b.w. of the blue dyestuff used in Example 2

are dissolved in

1400.0 p.b.w. of ethylene glycol monoethyl ether.

A series of such solutions are mixed in each case either with 5.0 parts by weight of the initiator numbered I 1 or the initiator numbered II 1, or with 5.0 parts by weight of a mixture of these two initiators.

The tests are carried out exactly as the tests described in Examples 2 and 3. The results are listed in the following Table VI.

TABLE VI

Initiators		Test No.	Number of Steps
Type I	Type II		
5.0 p.b.w.		39	1
4.0 p.b.w.	1.0 p.b.w.	50	8
3.0 p.b.w.	2.0 p.b.w.	51	9
2.5 p.b.w.	2.5 p.b.w.	45	10
2.0 p.b.w.	3.0 p.b.w.	52	11
1.0 p.b.w.	4.0 p.b.w.	53	10
0.5 p.b.w.	4.5 p.b.w.	54	9
0.25 p.b.w.	4.75 p.b.w.	55	8
	5.0 p.b.w.	44	1

## Example 5.

In this example, compounds according to Formula I carrying different substituents in the 10-position are compared.

5 140.0 p.b.w. of a copolymer of 87.5 p.b.w. of methyl methacrylate and 12.5 p.b.w. of methacrylic acid with an average molecular weight of 35,000,  
140.0 p.b.w. of trimethylol ethane triacrylate, and  
1.5 p.b.w. of the blue dyestuff described in Ex. 2  
are dissolved in

10 1400.0 p.b.w. of ethyleneglycol monoethyl ether.

A series of such solutions are mixed either with 5.0 p.b.w. of one initiator, or with 2.5 p.b.w. each of two initiators.

The samples are evaluated as in Example 1 and the results are listed in the following Table VII.

TABLE VII

Initiators		Test No.	Number of Steps
Type I	Type II		
I 18		56	1
I 18	II 1	57	9
I 29		58	no image
I 29	II 1	59	4
I 31		60	1
I 31	II 1	61	6
	II 1	62	1

## Example 6.

15 This example serves to illustrate that even in light-sensitive copying compositions containing multiply unsaturated high molecular weight compounds the synergistic effect of the initiator systems according to the present invention is fully effective.

20 A series of solutions are prepared comprising  
360.0 p.b.w. of diallyl isophthalate prepolymer and  
90.0 p.b.w. of pentaerythritol triacrylate in  
2900.0 p.b.w. of 2-methyl-2-methoxypentanone-4.

25 Each of these solutions is mixed either with 16.0 p.b.w. of a single initiator, or with 8.0 p.b.w. each of the two initiators of Formula I and Formula II to be used in mixture, and the solutions are then agitated until the solid substances have completely dissolved. The solutions are filtered and whirler-coated, at 100 revolutions per minute, onto a mechanically roughened aluminum foil. The coated aluminum foils are dried for 15 minutes at 50°C. and are then exposed in a vacuum frame under a 21-step half-tone step wedge (Kodak: Photographic Step Tablet No. 2), using an 8000 W xenon spot arc lamp from a distance of 72 cm.

30 After exposure, the samples are bathed for 60 seconds in 1,1,1-trichloroethane and then sprayed with clean solvent. The plates are then treated for 45 seconds, with the aid of a cotton pad, with the etching solution described in German Offenlegungsschrift No. 1,940,280 and comprising:

35 80.0 p.b.v. of gum arabic (14°Be),  
12.0 p.b.v. of phosphoric acid (85%)  
0.2 p.b.v. hydrofluoric acid (50%),  
0.5 p.b.v. of H<sub>2</sub>O<sub>2</sub> (30%), and  
40 7.3 p.b.v. of water.

The image areas are then inked up with greasy ink. The relative light-sensitivities are compared in the same manner as described in Example 1.

The results of the evaluation are listed in the following Table VIII.

TABLE VIII

Type I	Initiators Type II	Test No.	Number of Steps
	II 1 (8.0 p.b.w.)	63	8
	II 1 (16.0 p.b.w.)	64	8
I 2		65	4
I 2	II 1	66	13
I 4		67	7
I 4	II 1	68	14
I 6		69	6
I 6	II 1	70	15
I 7		71	5
I 7	II 1	72	13
I 8		73	8
I 8	II 1	74	13
I 9		75	8
I 9	II 1	76	15
I 12		77	3
I 12	II 1	78	14
I 13		79	3
I 13	II 1	80	13
I 15		81	8
I 15	II 1	82	15
I 16		83	7
I 16	II 1	84	16
I 17		85	7
I 17	II 1	86	15
I 24		87	3
I 24	II 1	88	13
I 29		89	3
I 29	II 1	90	13
I 30		91	1
I 30	II 1	92	14
I 33		93	6
I 33	II 1	94	16



## Example 7.

The solution described in Test 32 (Table IV) comprising  
140.0 p.b.w. of a copolymer of 85 p.b.w. of methyl methacrylate and 15 p.b.w. of methacrylic acid,

5 140.0 p.b.w. of trimethylol ethane triacrylate, 5  
1.5 p.b.w. of the blue dyestuff described in Ex. 2,  
2.5 p.b.w. of Compound I 18, and  
2.5 p.b.w. of Compound II 14, in

10 1400.0 p.b.w. of ethylene glycol monoethyl ether, 10  
is filtered and whirler-coated, at 100 revolutions per minute, onto an electrochemically roughened and anodized aluminum foil.

The coated plate is dried in a circulating-air dryer and is then again coated with the aqueous solution of polyvinyl alcohol and sodium lauryl ether sulfate described in Example 2 and dried.

15 After exposure under a negative original in an 8 kW xenon exposure apparatus 15  
from a distance of 72 cm, the plate is developed with the aid of a cotton pad, using the alkaline developer solution described in Example 1 containing sodium metasilicate, polyethyleneglycol 6000, levulinic acid, and strontium hydroxide in water. After wiping over with 1% phosphoric acid solution, the image areas of the  
20 plate are inked up with greasy ink. 20

The planographic printing plate thus produced may be used for printing several tens of thousands of flawless prints in an offset machine.

## Example 8.

25 A solution of 25  
140.0 p.b.w. of a copolymer of 85 p.b.w. of methyl methacrylate and 15 p.b.w. of methacrylic acid (molecular weight approximately 43,000),

140.0 p.b.w. of trimethylol ethane triacrylate,  
1.6 p.b.w. of the blue dyestuff used in Ex. 2,  
2.5 p.b.w. of Compound I 9, and  
30 2.5 p.b.w. of Compound II 2 in 30  
1400.0 p.b.w. of ethyleneglycol monoethyl ether

is filtered and whirler-coated, by means of a centrifuge, onto the chromium surface of a brass plate provided with a dull chromium plating, whereupon the plate is dried.

35 The plate is then coated with the aqueous solution of polyvinyl alcohol and sodium lauryl ether sulfate described in Example 2 and dried again. 35

40 After a 2 minutes' exposure under a positive original in a copying frame (using an 8 kW xenon spot arc lamp from a distance of 72 cm), the plate is developed with the aqueous alkaline developer solution used in Example 1, by wiping with a cotton pad. 40

Subsequently, the plate is etched with a commercially available chromium etch consisting of 42.4% of  $\text{CaCl}_2$ , 9.8% of  $\text{ZnCl}_2$ , 10.8% of  $\text{HCl}$ , and 37% of  $\text{H}_2\text{O}$  so that the chromium layer is etched away within two minutes. After rinsing with water, the copying layer is removed by immersion of the plate in acetone, the image is rinsed again, wiped over with 1% dilute  $\text{H}_3\text{PO}_4$ , and finally inked up with greasy ink. 45

A flawless multi-metal printing plate for planographic printing is obtained from which very long runs may be printed.

## Example 9.

50 In Example 12 of German Offenlegungsschrift No. 2,203,732, there is described the preparation of a photo-crosslinkable compound obtained from poly- 50  
(methyl vinyl ether/maleic anhydride) and allyl amine.

600.0 p.b.w. of this polymer,  
100.0 p.b.w. of trimethylol ethane triacrylate,  
55 8.0 p.b.w. of Compound I 1, and 55  
8.0 p.b.w. of Compound II 1

are dissolved in

1400.0 p.b.w. of methyl ethyl ketone,  
and the solution is applied to a "Nylon" fabric (about 80 meshes per centimeter) and dried. The coated fabric is image-wise exposed for 4 minutes under a positive original, using an 8 kW xenon lamp at a distance of 72 cm, and the resulting image is developed with acetone. A useful silk screen is thus obtained. 60

## Example 10.

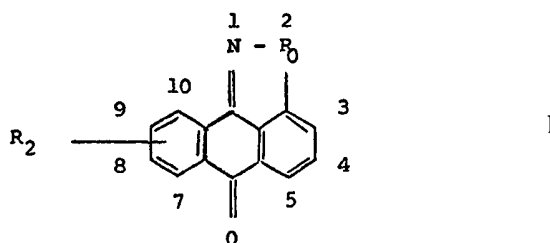
- A coating solution is prepared from
- 400.0 p.b.w. of styrene/maleic anhydride copolymer,
  - 200.0 p.b.w. of an  $\alpha$ -methylstyrene/vinyltoluene copolymer,
  - 25.0 p.b.w. of a polyvinyl butryal with an average molecular weight of 30,000 to 35,000,
  - 500.0 p.b.w. of trimethylol propanetriacrylate,
  - 1.0 p.b.w. of Compound I 1, and
  - 4.0 p.b.w. of Compound II 1, in
  - 2000.0 p.b.w. of methyl ethyl ketone and
  - 200.0 p.b.w. of ethyleneglycol monoethyl ether
- and filtered.
- A 35  $\mu$ m thick copper foil laminated to a base of phenolic resin paper is coated with this solution. After drying, the layer is covered with a 1 to 2  $\mu$ m thick polyvinyl alcohol layer.
- The coated copper plate is exposed for 2 minutes under a negative original showing a circuit diagram, using an 8 kW xenon lamp. Then it is developed with the aqueous alkaline developer used in Example 1 and etched at 50°C with an aqueous FeCl<sub>3</sub> solution.
- The copper is etched away in the bared areas and a printed circuit of the type used in the electrical industry is obtained.

## Example 11.

- 700.0 p.b.w. of a terpolymer of 25 p.b.w. of methacrylic acid, 62.5 p.b.w. of n-hexylmethacrylate, and 12.5 p.b.w. of methylmethacrylate as a binder,
  - 560.0 p.b.w. of the monomer described in Ex. 1 of German Offenlegungsschrift No. 2,064,079 (reaction product of 2,2,4-trimethylhexamethylene-diisocyanate and  $\beta$ -hydroxy-ethylmethacrylate),
  - 15.0 p.b.w. of triethyleneglycol dimethacrylate,
  - 2.0 p.b.w. of the blue dyestuff used in Ex. 2,
  - 5.0 p.b.w. of Compound I 28, and
  - 5.0 p.b.w. of Compound II 6
- are dissolved in
- 2500.0 p.b.w. of methyl ethyl ketone and
  - 200.0 p.b.w. of ethyl alcohol.
- The solution is filtered and coated onto a polyethylene terephthalate support in such a manner that the resulting dry layer weighs 32 g/m<sup>2</sup>.
- By means of a commercially available laminating apparatus, the coated film is laminated onto the copper surface of a composite material consisting of layers of copper and hard paper.
- After a two minutes' exposure of the laminate (xenon lamp, 8 kW) under a positive original showing a circuit diagram, the protective film is pulled off and the image of the circuit diagram is developed with a 0.8 per cent strength sodium carbonate solution.
- The copper circuit paths are reinforced by electrodeposition and then covered, also by electrodeposition, with a lead-tin layer.
- The resist layer is removed by immersion in acetone. Finally, the bared copper is etched away in a FeCl<sub>3</sub> solution, thus completing the photochemical production of a printed circuit.
- In our copending Application No. 54130/76 (Serial No. 1,576,218) there is disclosed and claimed a light-sensitive composition comprising an ethylenically unsaturated polymerizable compound, a photoinitiator of the formula I, as given above, and optionally a binder.

## WHAT WE CLAIM IS:—

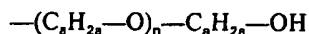
1. A light-sensitive composition comprising at least one ethylenically unsaturated compound with at least two double bonds capable of addition polymerization, other than a compound of the formula II, and a photoinitiator system comprising at least one compound of the general Formula I



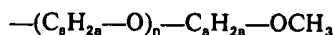
wherein

$R_0$  is O, S or  $NR_1$ ,

$R_1$  denotes hydrogen, a saturated or unsaturated unsubstituted hydrocarbon radical with 1 to 6 carbon atoms, an aralkyl group with 7 to 10 carbon atoms, an acyl group with 2 to 18 carbon atoms, an amidomethylene group, an aminocarbonyl group with from 2 to 11 carbon atoms, a polyalkyleneoxide group of the general formula

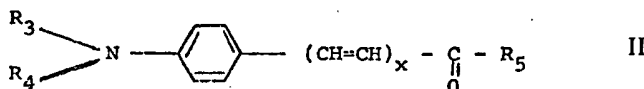


or the general formula



wherein  $a=2$  to 4 and  $n=1$  to 10, or a saturated or unsaturated hydrocarbon radical with 1 to 6 carbon atoms which is substituted by hydroxyl, alkoxy, alkoxycarbonyl, acyl, acyloxy, and/or halogen,

$R_2$  is hydrogen, an alkoxy group, an alkyl group with 1 to 6 carbon atoms, or halogen, and at least one compound of the general Formula II



wherein

$R_3$  is an alkyl group with 1 to 6 carbon atoms,

$R_4$  is an alkyl group with 1 to 6 carbon atoms, and

$R_5$  is hydrogen, an alkyl group with 1 to 6 carbon atoms, an alkoxy group in which the alkyl group has 1 to 4 carbon atoms, an aryl group with 6 to 12 carbon atoms, or a dialkyl amino styryl group, and wherein

$x$  is 0 or 1, and optionally, at least one polymeric binder.

2. A composition as claimed in claim 1, wherein the double bonds in at least one ethylenically unsaturated compound are terminal double bonds.

3. A composition as claimed in claim 1 or claim 2 wherein the initiator comprises at least one of the specific compounds of the general formula I mentioned herein.

4. A composition as claimed in any one of claims 1 to 3 wherein the initiator comprises at least one of the specific compounds of the general formula II mentioned herein.

5. A composition as claimed in any one of claims 1 to 4 wherein the compounds of the general formula I and general formula II are present in a weight ratio of from 2:98 to 98:2.

6. A composition as claimed in any one of claims 1 to 5 comprising, as a polymerisable compound, an acrylic or methacrylic acid ester.

7. A composition as claimed in claim 6 comprising at least one of the acrylic or methacrylic esters specified herein.

8. A composition as claimed in any one of claims 1 to 7 comprising, as a polymerisable compound, a high molecular weight, polyunsaturated, polymerisable compound.

9. A composition as claimed in any one of claims 1 to 8 which contains a polymeric binder which is softenable or soluble at room temperature in an aqueous alkaline solution.

10. A composition as claimed in claim 9 wherein the binder comprises a styrene/maleic anhydride copolymer, an alkyl methacrylate/methacrylic acid copolymer or a maleate resin.
- 5 11. A composition as claimed in any one of claims 1 to 10 comprising a thermal polymerisation inhibitor. 5
12. A composition as claimed in claim 1 substantially as described in any one of tests 9 to 23, 32 to 38, 45 to 49, 50 to 55, 57, 59, 61, 66, 68, 70, 72, 74, 76, 78, 80, 82, 84, 86, 88, 90, 92 and 94 herein or in any one of Examples 7 to 11 herein.
- 10 13. A composition as claimed in any one of claims 1 to 12 in the form of a solution or dispersion. 10
14. A composition as claimed in any one of claims 1 to 13 in the form of a solid layer on a carrier.
- 15 15. A composition as claimed in claim 14 wherein the carrier comprises aluminium, magnesium, zinc, copper, steel or a plastics material. 15
16. A composition as claimed in claim 14 or claim 15 wherein the surface of the layer remote from the carrier has thereon an oxygen-impermeable protective layer.
17. A composition as claimed in claim 14 substantially as described in any one of the Examples herein.
- 20 18. A method of making an article comprising at least the steps of image-wise exposing to actinic light a composition according to claim 16 and then processing the exposed composition in order to remove either the exposed portions or the unexposed portions of the layer. 20
19. A method as claimed in claim 18 wherein the exposed composition is treated with a liquid developer to dissolve or soften the unexposed portions of the layer.
- 25 25
20. An article whenever made by the method of claim 18 or claim 19.
21. An article as claimed in claim 20 which is a printing forme.
22. An article as claimed in claim 20 which is a printed circuit board.

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